
Chapter 3. General Description of Steam Injection

3.1. NAPL Source Zones and Plume Longevity

The release of man-made chemicals in the form of non-aqueous phase liquids (NAPL) to the subsurface has resulted in persistent ground water contamination. The natural attenuation of NAPL contamination in soil and ground water is slow, resulting in typical plume lives of hundreds to thousands of years. The longevity of NAPL source zones is primarily caused by the environmental stability of the NAPL, its low mobility in soils, slow dissolution rate into moving ground water, and low vaporization rate when located below the ground water table (Hunt et al., 1988a; Mercer and Cohen, 1990; Pankow and Cherry, 1996). This stability in the environment, combined with aqueous solubilities of NAPL constituents, which are typically orders of magnitude higher than the acceptable ground water concentrations, leads to ground water contamination problems that can persist for centuries (Hunt et al., 1988a).

Conventional in-situ remediation techniques applied in unconsolidated media involve fluid injection and extraction at ambient temperature as a means of removing the NAPL from the subsurface environment. However, once NAPL finds its final distribution after the spill occurs it is relatively immobile, and flushing with water and air has limited effect on its mobility. For NAPL found below the water table, remediation approaches employing flushing suffer from mass-transfer limitations due to the characteristically low diffusivities of the constituents in water and the presence of NAPL in regions not in contact with the flowing fluids. The Steam Enhanced Remediation (SER) process was designed to overcome these mass-transfer limitations, and to provide a relatively rapid source removal and aquifer restoration option.

The fractured rock environment creates additional challenges for remediation due to the dual porosity and permeability of the fracture/matrix systems, the potentially limited interconnectivity of fracture networks, and the sequestering of contaminants in the low permeability rock matrix. Currently, no remediation technologies have been proven to be successful in fractured rock, and indeed, few attempts have been made to remediate contaminants in fractured bedrock, despite the fact that a large number of contaminated sites have been identified where at least part of the contamination exists in fractured rock.

3.2. Steam Enhanced Remediation Technology Background

While steam injection for enhanced oil recovery has been practiced for decades by the oil industry (Ramey, 1966; Mandl and Volek, 1969; Volek and Pryor, 1972; Konopnicki et al., 1979), its use for environmental remediation was not considered until the 1980s. The first reported use of steam injection for remediation was a pilot study to remove petroleum hydrocarbons from soils in the Netherlands (Hilberts et al., 1986). The first use of steam to address chlorinated solvent contamination in the subsurface was a pilot study in California in 1988 (Udell and Stewart, 1989). Building on the findings of that second study, additional thermodynamic features of the process were identified and exploited to make the process amenable to the restoration of sites contaminated with volatile and semi-volatile liquid contaminants found above and below the water table, as well as non-volatile compounds in the aqueous phase (Udell et al., 1991; Udell and Stewart, 1992).

The in-situ process using steam injection and aggressive fluids extraction has been called Steam Enhanced Extraction (Udell et al., 1991), Steam Remediation, and Dynamic Underground Stripping. For consistency, the process name “Steam Enhanced Remediation,” or SER, has been adopted in this report.

The mechanisms leading to the mobilization of contaminants in unconsolidated media by steam injection were studied intensively in laboratory experiments and theoretical investigations (Hunt et al., 1988b; Stewart and Udell, 1988; Basel and Udell, 1989; Yuan and Udell, 1993; Sleep and Ma, 1997; Imhoff et al., 1997), and are summarized by Udell (1996) and Davis (1998).

More recently, the co-injection of air during steam injection has been tested and applied both in laboratory studies (Betz et al., 1998; Schmidt et al., 2002; Kaslusky and Udell, 2002) and in the field (IWR, 2003; Earth Tech and SteamTech, 2003; SteamTech, 2003). The injection of air enhances vapor transport between injection and extraction points and reduces the risk of NAPL condensation bank formation that may lead to downward NAPL mobilization. At the recent full-scale remediation at the Young-Rainey STAR Center in Pinellas, Florida, air injection was used to optimize vadose zone remediation by creating a horizontal sweep of vapor, and to assist in venting and controlling cool-down after cessation of steam injection (U.S. DOE, 2003; Heron et al., 2005).

3.3. Thermal Remediation Mechanisms

The steam enhanced extraction process removes volatile and semivolatile contaminants from the subsurface by heating the soil to volatilize them, while displacing mobile liquids (ground water and NAPL) ahead of the advancing steam zone. Liquids displaced by the injected steam are pumped from extraction wells. The vapors containing the volatilized contaminants are captured by vacuum extraction. Once they are above ground, extracted ground water and vapors are cooled and condensed. Liquid hydrocarbons are separated from the aqueous stream for recycling, and process vapors and water are treated before discharge.

Heating the subsurface to temperatures near the boiling point of water leads to dramatic changes in the thermodynamic conditions, and makes NAPL much more mobile. The major effects are:

- The vapor pressure of volatile and semivolatile compounds increases markedly with temperature. As the subsurface is heated from 20°C (68°F) to an average temperature of 100°C (212°F), the vapor pressure of the contaminants will increase by between 10 and 30-fold (Udell, 1996).
- Boiling of co-located NAPL and water phases will occur at temperatures below the boiling point of water (DeVoe and Udell, 1998; Heron, 1998b).
- Adsorption coefficients are reduced by heating, leading to release of contaminants from the soil or rock matrix (Heron et al., 1998a; Sleep and McClure, 2001).
- Viscosity of NAPLs is reduced by heating. The higher the initial viscosity, the greater the reduction. For moderately viscous NAPL, viscosity can be reduced by approximately an order of magnitude by heating from ambient to steam temperature (Davis, 1997). For TCE and other chlorinated solvents, the viscosity typically is reduced by about a factor of two (Heron et al., 1998b).
- DNAPL density is reduced during heating, which improves its flotation and displacement. For chlorinated solvents, the effect is modest, with less than 10 percent swelling of the DNAPL. For DNAPLs such as creosote, the density changes can cause a DNAPL to become less dense than water, aiding in its recovery as an LNAPL (Davis, 2002).
- NAPL-water interfacial tensions for some NAPLs are lowered by as much as two-fold, allowing for improved hydraulic removal of NAPLs (Davis, 1997; She and Sleep, 1998).
- Water solubility increases for organic contaminants at elevated temperatures, while dissolution rates increase by factors of two to five, leading to faster NAPL dissolution and removal (Sleep and Ma, 1997; Imhoff et al., 1997).

These physical effects provide several pathways by which the NAPL is removed from the subsurface:

- Displacement as a NAPL phase and extraction with the ground water (Hunt et al., 1988b; Udell et al., 1997).
- Vaporization and extraction in the vapor phase.
- Volatilization, migration in the steam phase, and condensation in water that is subsequently removed by pumping.
- Dissolution and desorption and removal with the extracted water.

For chlorinated solvents such as PCE, vaporization is believed to be the most important mechanism for recovery, and most of the contaminants are extracted in the vapor phase (typically between 80 and 95 percent). As the contaminants become less volatile, liquid phase recovery becomes more important. For example, approximately 50 percent of the creosote recovered from the Visalia Pole Yard by steam injection was as a NAPL, and approximately equal amounts were recovered in the vapor and aqueous phases (Eaker, 2003).

In addition to the physical removal described above, biological and chemical degradation mechanisms may occur during and after thermal remediation. These mechanisms include:

- Microbial degradation of NAPL components (Newmark and Aines, 1997).
- Abiotic oxidation reactions which occur in water at elevated temperature in the presence of oxygen. These reactions have been called Hydrous Pyrolysis/Oxidation, and may provide some destruction of contaminants such as creosote under certain conditions (Leif et al., 1998; Davis, 2002).
- Hydrolysis at elevated temperature. This is particularly relevant for chemicals with short half-lives such as methylene chloride and 1,1,1-trichloroethane (Jeffers et al., 1989).

Field-scale thermal remediation should be designed to use a combination of the mechanisms listed above. Since contaminants can be effectively mobilized as a liquid NAPL, as a vapor, and as dissolved phases, capture and control of the fluids are essential for successful remediation.

3.4. Steam Injection Demonstrations and Remediations in Unconsolidated Media

Numerous field demonstrations and several full-scale remediations using SER have been completed. The first such demonstration was conducted in 1988 at a solvent recycling facility in San Jose, California (Udell and Stewart, 1989). Steam was injected into the vadose zone in an area containing residual solvents for five days. After heating to near steam temperatures, steam was injected in a cyclic mode in order to induce pressure changes, which is referred to as pressure cycling (Udell et al., 1991; Itamura and Udell, 1995). Pressure cycles were induced by temporarily turning off the steam to the injection wells while continuing to extract ground water and vapors. This led to pressure drops in the formation, which created in-situ boiling and led to extraordinary recovery rates. Typically, 90 percent of the mass in the treatment zone in high permeability regions was removed in that short time frame, although higher solvent concentrations remained in low permeability regions and zones not sufficiently heated.

The second demonstration was conducted at full-scale at the Lawrence Livermore National Laboratory in 1993 (Newmark, 1994; Newmark and Aines, 1997). Nearly 30,000 liters (7,600 gallons) of gasoline were removed from the subsurface, including significant volumes from deep zones 9 meters (30 feet) below the water table. The remediation was conducted over a period of six months, using SER in combination with electrical heating of low permeability zones and electrical resistance tomography (ERT) to monitor steam and hot water movement. The combination of these technologies has been called Dynamic Underground Stripping. In 1996, California regulators confirmed that no further remedial actions were required for the hydrocarbon-contaminated ground water.

The third demonstration was a pilot test at Naval Air Station Lemoore, California, in 1994 (Udell and Itamura, 1995). Almost 300,000 liters (78,300 gallons) of less volatile JP-5 were removed from the subsurface over a period of three months. JP-5 soil concentrations dropped from over 50,000 milligrams per kilogram (mg/kg) to below 10 mg/kg at the location of the water table.

In contrast to these successful demonstrations, other steam injection projects have been completed that did not include the cyclic polishing step, and have been only moderately successful. At the Rainbow Disposal transfer yard in Huntington Beach, California, steam injection was applied to recover diesel fuel with lesser success due to inadequate injection rates and subsurface temperature monitoring (U.S. EPA, 1995). At Hill Air Force Base, Utah, short periods of steady steam injection followed by air injection were applied at a solvent spill site and at an isolated treatment cell containing DNAPL with moderate success (Gildea and Stewart, 1997).

Field demonstrations employing pressure cycling continued in the late 1990's (BERC, 2000; Heron et al., 2000). The Alameda Point demonstration removed about 2,300 liters (600 gallons) of NAPL from a small source area, with overall soil and water VOC concentration reductions in the order of 1,000-fold. The demonstration lasted 70 days, and the results were highly promising for restoration of TCE-rich source zones in shallow unconsolidated soils.

Mass removal of TCE and PCE was demonstrated at the Savannah River Site, South Carolina (IWR, 2002; Oochs et al., 2003). However, post-operational data on soil and ground water quality are not available to assess whether complete aquifer restoration occurred.

Recently, a large, full-scale remediation of a creosote-contaminated site in Visalia, California was completed (Newmark and Aines, 1998; Eaker, 2003). Approximately 590,000 kg (1,300,000 lbs) of wood-treating chemicals were removed from the subsurface during three years of steam injection. Post treatment soil sampling showed significant reductions in creosote concentrations, and ongoing ground water sampling shows aqueous creosote concentrations are continuing to decline. In 2003, ground water samples at the downgradient edge of the property showed pentachlorophenol and benzo(a)pyrene concentrations near or below the cleanup goal.

In 2003, SteamTech completed a full-scale DNAPL site restoration at the Young-Rainey STAR Center, Florida (SteamTech, 2003). This clean-up involved steam and air injection at 36 wells, electrical heating of a bottom clay layer, and fluid extraction from 28 wells. More than 1,360 kg (3,000 lbs) of VOC chemicals were removed in a period of 4.5 months, with post-operational sampling showing that less than 0.5 kg (1 lbs) of VOCs remained in the subsurface. Pressure cycling and air injection were deemed very effective in shortening the remediation time. The highest post-operational ground water concentration in the 48 samples collected was ten times the maximum concentration level (MCL) for TCE; most samples were nondetect. Comparing soil concentrations before and after the remediation showed an average VOC concentration reduction of 99.93 percent (Heron et al., 2005). This result confirmed the assumption that SER can be completely effective for restoring unconsolidated media aquifers contaminated by VOCs to near MCL concentrations.

Overall, SER is now a well-documented technique for NAPL source reduction in unconsolidated media, both above and below the water table. Implemented properly, not only source zone removal, but also restoration – i.e., reduction of contaminants to very low soil and ground water concentrations – are possible.

3.5. Steam Demonstrations in Fractured Rock

NAPL contamination occurring in fractured rock aquifers is common in the United States and in many other areas around the world. In fractured rock, steam migration, and thus the remedial success, is much less predictable. The location of the permeable fractures is typically not accurately known, and connectivity between injection and extraction wells cannot be assumed, as in unconsolidated media. Thus, the design of individual wells and of the overall well-field is a major challenge when transferring steam remediation technology to fractured rock.

The remediation of a TCE source in fractured rock using SER was completed in 2001 at a site near Prague, Czech Republic (Dusilek et al., 2001). The approach was to remove the DNAPL source by vaporization and entrainment of resulting TCE vapors by injecting air, which was recovered by soil gas extraction. The site has three main geologic features: a 6-meter (20-feet) thick permeable near-surface zone comprised of highly fractured sandstone and containing perched water; a 1-meter (3-feet) thick claystone rock aquitard; and a deep, 1.8-meter (6-feet) thick aquifer comprised of highly fractured sandstone. Each unit appeared to be contaminated by NAPL TCE.

Steam and air were first injected into two wells beneath the NAPL source zone, and vapors were extracted from a series of dual-phase extraction wells surrounding the injection wells. After the bottom aquifer was sufficiently heated, steam and air were injected into the upper permeable zone. When both aquifers were heated, air injection was ceased while continuing with pure steam injection. Once the aquifer and aquitard system were heated to the temperature equal to the local boiling point of water, the site was depressurized and then re-pressurized in a cyclical manner to reduce the concentrations of aqueous phase contaminants. Post-steaming ground water analysis in regions treated by SER showed reductions in ground water concentrations from greater than 100 milligrams/liter (mg/l) to less than 0.10 mg/l (Dusilek et al., 2001).

In 2002, SER was field tested at Site 61 at Edwards Air Force Base, California (Earth Tech and SteamTech, 2003). This treatability study used a five-well layout with a single steam injection well surrounded by four extraction wells. The source zone consisted of fractured granite bedrock contaminated with TCE and diesel-range organics. This 45-day field test resulted in the removal of between 900 and 1,800 kg (2,000 and 4,000 lbs) of chemicals, including NAPL. Post-operational sampling showed nondetect soil concentrations in all samples collected above the water table, and reductions of ground water TCE concentrations in the range of 50 to 90 percent. The test was deemed highly successful for the vadose zone source removal. However, the test was not continued long enough to heat the aquifer to near steam temperatures, and thus, no conclusions could be drawn on aquifer restoration efficacy in fractured granite. Pressure cycling and air injection proved beneficial for increasing the chemical mass removal rate by at least a factor of two when compared to continuous steam injection and extraction.

Despite the positive results in unconsolidated media and at the two fractured rock sites addressed prior to this project, the applicability of SER at a site such as the Loring Quarry could not be assured. To the best of our knowledge, no SER demonstration has been completed in such a complex, tight, and sparsely fractured limestone. The depth of DNAPL contamination at Loring Quarry apparently exceeds 21 meters (70 feet), which is at least 17 meters (55 feet) below the water table. At these depths, the limestone fractures are of relatively small apertures (less than 2×10^{-4} meters (6.6×10^{-4} feet)), and very sparse (typically less than one fracture was encountered per meter (3 feet) of core collected). This makes the Loring Quarry much more challenging for SER than the sites treated previously.